

Photoabsorption spectrum of the Xe@C₆₀ endohedral fullerene

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ABSTRACT

Photoabsorption spectrum of the Xe@C₆₀ endohedral fullerene has been studied using the time-dependent-density-functional-theory (TDDFT), which represents the dynamical polarizability of an interacting electron system by an off-diagonal matrix element of the resolvent of the Liouvillian superoperator and solves the problem with the Lanczos algorithm. The method has been tested with the photoabsorption cross sections of the free Xe atom and C₆₀ fullerene. The result for the Xe@C₆₀ confirms the three main peaks observed in the recent measurement in the energy region of the Xe *4d* giant resonance and demonstrates the underestimation of the photoionization cross section by the experiment. It is suggested to use the current theoretical result around 22 eV to calibrate the experimental data.

PACS:33.80Eh, 31.25.Qm

1 Introduction

Photoabsorption and photoionization cross sections of the Xe@C₆₀ molecule have been studied extensively by many groups both theoretically [1, 2, 3, 4, 5] and experimentally [6]. Puska and Nieminen [1] modeled for the first time the C₆₀ molecule using a spherical shell with an attractive potential and used a jellium shell to calculate the 4d photoabsorption cross section of a Xe atom inside the C₆₀ molecule. Their result demonstrated some oscillations in the cross section curve. Amusia and co-workers [2, 3, 4] used a δ -like potential for the C₆₀ shell and the random-phase approximation with exchange (RPAE) method to describe the photoionization process. Their results indicate that the giant resonance is distorted substantially, exhibiting four prominent peaks [3]. Dolmatov and Manson [5] showed that two of those peaks disappear if the finite thickness of the C₆₀ cage is utilized. However, their result is not supported by the recent experiment [6]. The experimental data demonstrate strong enhancement of the photoionization cross section as well as an oscillatory structure of the amplitude. The complicated experimental resonance structure is also quite different from the calculation of the time-dependent density-functional theory (TDDFT) [7], which considers all the valence electrons to form a delocalized charged cloud and treats the residual ion-core as a classical jellium shell. Recently, Chen and Msezane performed a calculation on the confinement resonance of the Xe@C₆₀. They solved the Schrödinger equation in three separate regions, $r < r_i$, $r_i < r < r_o$ and $r > r_o$ using both regular and irregular solutions, where r_i and r_o are, respectively the inner and outer radii of the C₆₀ spherical shell. The RPAE method was utilized to describe the photoionization process. This method has been successfully used in the study of the photoionization of the encapsulated Ce³⁺ [8, 9] and Xe⁺ [10] ions in C₆₀. For the photoionization of the Xe@C₆₀ molecule they obtained an improved agreement between theory and experiment [11]. Although the photoionization of the Xe@C₆₀ molecule

has been studied using various theoretical models, however, a first principle calculation is still needed.

In this paper we have performed a time-dependent density-functional-theory (TDDFT) calculation for the photoabsorption spectrum of the Xe@C₆₀. The calculations of the optical spectra are carried out in the linear response formalism. The most widespread calculation of the electronic excitation in TDDFT is the Casida’s approach [12], which reformulated the calculation of the response function into a generalized Hermitian eigenvalue problem. However, this method is not suitable for calculating the spectra in a broad energy range. Recently a method has been developed, which determines the dipole susceptibility based on the application of the Lanczos algorithms to the first order expansion of the time-dependent Kohn-Sham equation in the linear response regime [13, 14, 15]. Here the absorption spectrum is calculated from the imaginary part of the dipole susceptibility. The method avoids the explicit calculation of the unoccupied states of the ground state and allows the entire spectrum of a molecule to be computed. This new implementation of the TDDFT has been used in the present Xe@C₆₀ calculation.

2 Method and results

We used the DMol₃ software of density-functional theory to determine the structures of the C₆₀ and Xe@C₆₀ and the TDDFT to evaluate the photoabsorption spectra.

The TDDFT method was used first to calculate the photoabsorption spectra of the C₆₀ fullerene. The C₆₀ geometry optimization was performed using the generalized gradient approximation (GGA) to the density-functional theory, with PBE exchange-correlation functional [16] along with all electron double numerical plus polarization (DNP) basis sets as implemented in the DMol₃ package [17]. The optimization of atomic positions proceeded until the change in energy was less than 5×10^{-4} eV and the forces were

less than 0.01 eV/Å. The resultant structure has the length of the shorter bond (hexagon-hexagon) 1.392 Å and the longer bond (hexagon-pentagon) 1.448 Å. These values are in good agreement with the x-ray data value of 1.391 Å for the shorter bond and 1.455 Å for the longer bond [18]. The structure was validated using a plane-wave approach as implemented in the QUANTUM-ESPRESSO [19]. A supercell of 18 Å was constructed to eliminate the interactions among cells. An ultrasoft pseudopotential of the Rappe-Rabe-Kaxiras-Joannopoulos (RRKJ) [20] type and a kinetic energy cutoff of 408 eV for the wave function and 2448 eV for the densities and potentials were employed in a standard ground state DFT calculation, yielding the Kohn-Sham eigenvalues and eigenvectors for all the occupied states. The dynamical polarizability of an interacting electron system is represented as an appropriate off-diagonal matrix element of the resolvent of a Liouvillian superoperator. The resolvent of the Liouvillian is evaluated through an algorithm based on the Lanczos method [13, 14, 15].

Fig 1 presents the photoabsorption spectrum for the C₆₀ after 3000 Lanczos iterations. Solid curve is from our TDDFT calculation and the dashed line represents the measurements [21, 22, 23]. The first three peaks at 3.48, 4.36, and 5.36 eV agree very well with the other TDDFT and local orbitals calculation [24]. Their results show the peaks at 3.5, 4.4, and 5.4 eV. The C₆₀ fullerene has a giant resonance, which corresponds to a collective oscillation of delocalized electrons relative to the ionic cage. The peak around 5-7 eV is the π plasmon resonances. The largest peak around 22 eV is related to the σ surface plasmon resonance, which was first predicted by the linear response theory [25]. The second collective resonance near 30-40 eV is associated with a dipole-excited volume plasmon [26]. Our solid curve shows the second volume plasmon resonance predicted by the experiment [26]. The overall excellent agreement has been obtained between our TDDFT result and the measurements.

The TDDFT method using the Liouville-Lanczos approach has also been

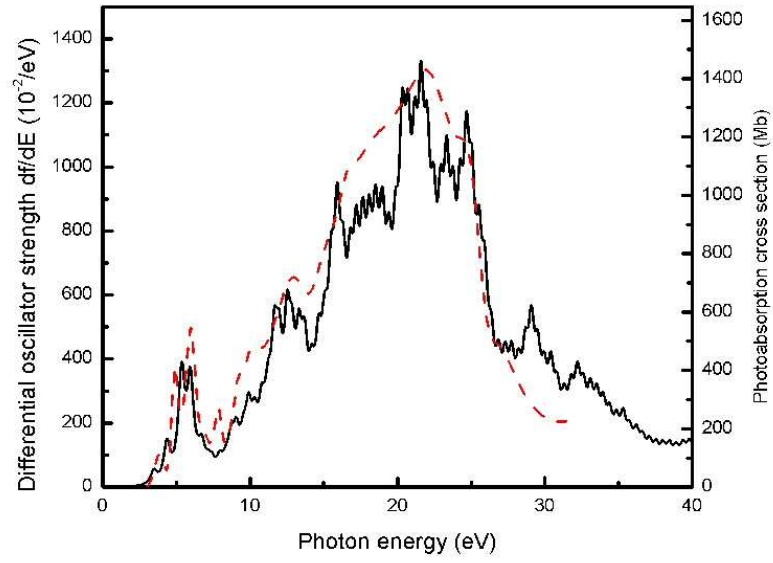


Figure 1: (Color online) Photoabsorption spectrum of C_{60} . Solid curve represents the result of the TDDFPT calculation. Dashed line are the experimental data [21, 22, 23]

used to evaluate the photoabsorption spectra for a free Xe atom. In order to study the 4d giant resonance of a Xe atom, an ultrasoft pseudopotential, which includes 4d electrons as valence electrons has been created using the `ld1.x` program of the QUANTRUM-ESPRESSO with the Xe ground state as the reference electron configuration. The pseudopotential has multiple-projector with PBE of GGA exchange-correlation functional and includes nonlinear core corrections. Fig. 2 shows the calculated photoabsorption spectra. Solid line is the calculated absolute differential oscillator strength of the photoabsorption of the Xenon atom in the energy region of 8.43 eV (5p threshold) -140 eV. Triangles are the experimental data obtained by Chan *et al* [27] using a low-resolution spectrometer. Solid squares and solid circles are respectively, the measured photoionization cross sections of the 4d subshell of Xenon atom by Holland *et al* [28] and Kämmerling *et al* [29]. Note that the unit of photoionization cross section on the right vertical coordinate is the Mb, which is related to the differential oscillator strength through, $1.0975 \text{ Mb} = 1 \times 10^{-2} \text{ differential oscillator strength unit (1/eV)}$ [30]. Our calculation describes those measured data very well.

The structure of the Xe@C₆₀ was obtained by adding a Xe atom into the center of the C₆₀ fullerene and then performing the same geometry optimization as that of the C₆₀. The kinetic energy cutoff of 1020 eV for the wave function and 4080 eV for the density were used in the ground state calculation. Fig. 3 shows the photoabsorption spectrum of the Xe@C₆₀. In the energy range of the Xe 4d giant resonance, we can find several small wiggles which do not exist in the C₆₀ case. The enlarged details of these wiggles are presented in Fig. 4. Fig. 4 also shows the convergence situations of the 4d resonance. Dotted line, dashed line and solid line represent, respectively the 1500, 3500 and 4500 Lanczos iterations.

Fig. 5 is the comparison of our TDDFT calculation with the experiment in the energy range of the Xe 4d giant resonance. Solid circles with the error bars are from experiment [6]. Solid curve represents our calculation. Since

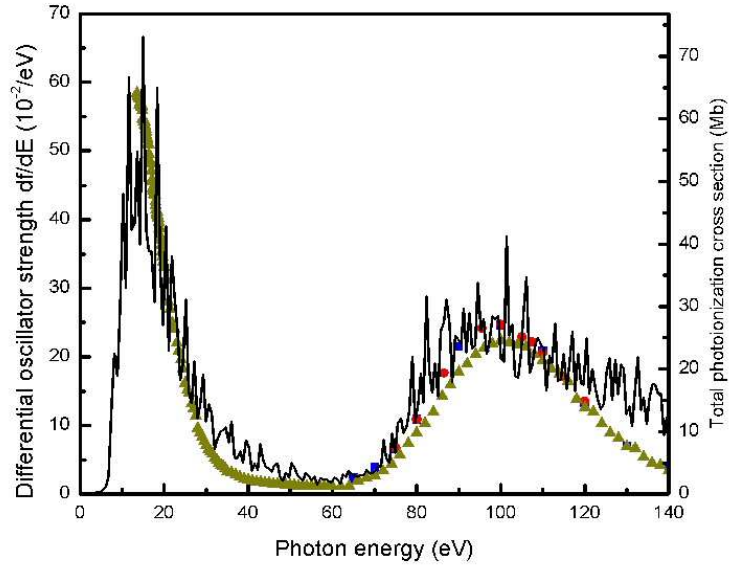


Figure 2: (Color online) Photoabsorption spectrum of free Xe atom. Solid curve is our TDDFT results. Triangles, solid squares and solid circles are respectively, from the measurements of [27], [28] and [29].

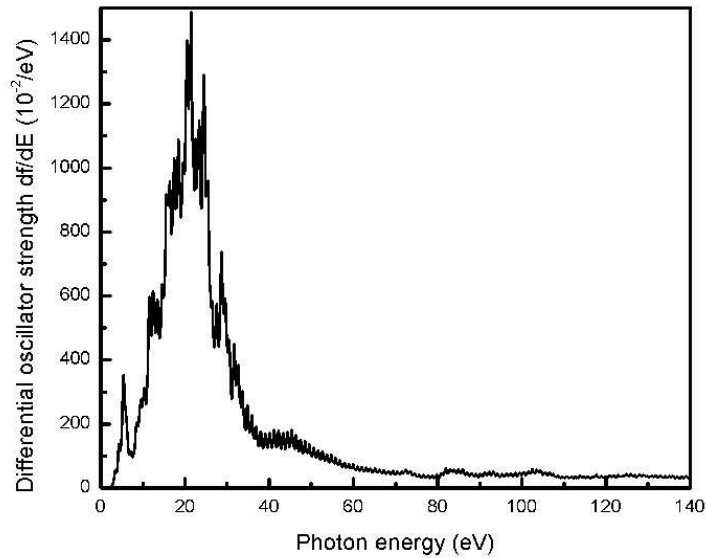


Figure 3: Photoabsorption spectrum of Xe@C₆₀

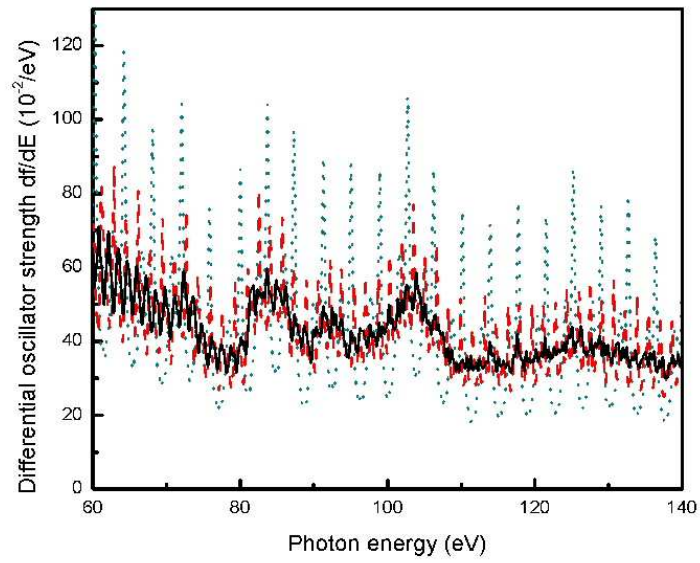


Figure 4: (Color online) Comparison between the spectra at different iterations. Dotted, dashed and solid curves represent, respectively 1500, 3500 and 4500 iterations.

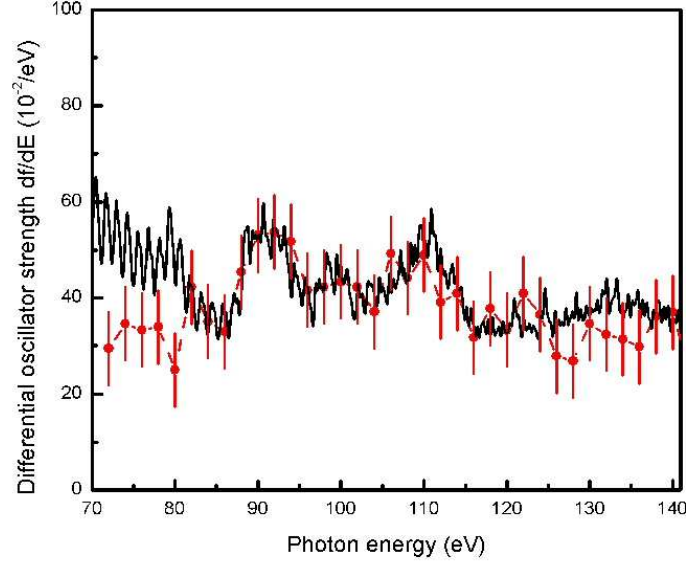


Figure 5: (Color online) Comparison between the TDDFT calculation and the experimental data. Solid circles with error bars are taken from Ref. [6]. Solid curve is our TDDFT calculation. Experimental data have been enlarged seven times and shifted upwards by $0.25/\text{eV}$. The calculated curve has been shifted to the right by 7 eV.

the experiment underestimates the photoionization cross sections we have enlarged the measured cross sections by a factor of seven and shifted them upwards by $0.25/\text{eV}$. The calculated Xe@C_{60} curve is shifted to the right by 7 eV to match the three main peaks of the experiment. Our calculation confirms the three main peaks in the measurement and demonstrates that the experiment has underestimated the photoionization cross section of Xe@C_{60} . We recommend the use of the TDDFT result at the low energy region to calibrate the measurement. For example, at 21.47 eV the photoionization cross section from TDDFT is 1633 Mb.

3 Conclusion

In conclusion, photoabsorption spectra for the Xe@C₆₀ molecule has been studied using the TDDFT method. The result confirms the three main peaks observed in the experiment [6]. The calculation also reveals the underestimation of the photoionization cross section by the measurement. It is suggested to use the TDDFT result around 22 eV to calibrate the measurement.

ACKNOWLEDGMENTS

This work was supported by the U.S. DOE, Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences, Office of Energy Research, AFOSR and Army Research Office (Grant W911NF-11-1-0194). Calculations used Kraken system of the National Institute for Computational Science, The University of Tennessee.

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